REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY) 13-04-2009	2. REPORT TYPE Final	3. DATES COVERED (From - To) 10/1/2005 – 9/30/2008

4. TITLE AND SUBTITLE

Potential Energy Surfaces and Dynamics of High Energy Species

5a. CONTRACT NUMBER
FA9550-06-1-0043

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Mark S. Gordon

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Iowa State University
Ames, Iowa 50011

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR, 875 North Randolph
Suite 325, Rm 3112
Arlington , VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSOR/MONITOR'S REPORT
NAFRL-OSR-VA-TR-2013-1039

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution Statement A: Approved for Public Release. Distribution is unlimited

13. SUPPLEMENTARY NOTES

20130918420

14. ABSTRACT

Several papers on ionic liquids have been published or submitted as a result of this grant. The first set of papers used second order perturbation theory to study the geometries and substituent effects of the cations commonly employed in energetic ionic liquids. These are variously substituted triazolium, tertazolium, and pentazolium cations. The heats of formation of all species were predicted using G2 and G3 theory. It was consistently found that the most energetic substituent's are –CN and –N_3. When one cation is combined with one anion, proton transfer almost always occurs with no intervening energy barrier, yielding a neutral pair. When two ion pairs are considered, conceptually similar to the face of a crystal, the ion separated species is predicted to be 6 kcal/mol lower in energy than the double proton transferred neutral species. These calculations were done using coupled cluster theory, but this level of theory is too expensive to study larger clusters. Therefore, we have turned to the fragment molecular orbital method, which can retain the accuracy of full electronic structure theory calculations, while greatly reducing the cost.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					19b. TELEPHONE NUMBER (include area code)

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Final Report

This is the final report for the High Energy Density Matter (HEDM) grant, FA9550-06-1-0043, "Potential Energy Surfaces and Dynamics of High Energy Species" that ended in Fall 2008.

Ionic Liquids. Several papers on ionic liquids have been published or are in press as a result of this grant:

1. Michael W. Schmidt, Mark S. Gordon, and Jerry A. Boatz, "Triazolium-Based Energetic Ionic Liquids", J. Phys. Chem., <u>A109</u>, 7285 (2005).

The results presented in this paper address several different aspects of energetic ionic liquids. The conclusions reached include the following:

A. The contribution of the two resonance structures in the unsubstituted triazolium cation is roughly equal, with approximately 3/2 p electrons found on both charged nitrogens. Substitution at ring nitrogen atoms produces little change in the extent of this charge delocalization, as shown by both very small geometry changes in the rings, and by MCSCF analysis of the resonance hybrids. The two substituent's that cause the most degradation to resonance are CN and NF_2, but to only a small extent. It appears that substitution will not hinder the ability of these captions to form ionic liquids.
B. A number of energetic and less energetic substituent's at the ring nitrogens were investigated, and in all cases 1,4 substituted triazoliums are lower in energy than 1,2 substituted triazoliums. There is a small energy preference for monosubstitution at N_1 over N_4 in the 1, 4 substituted triazoliums. The heats of formation for substituted gas phase triazolium captions were presented, and the CN substituent is suggested as a synthetic target, over N_3, since the former does not require creating a ring *exo* NN bond, but rather a NC bond.
C. Triazolium dinitramide systems are rich in structure. The numerous geometries and their relative energies are understandable by consideration of hydrogen bonds and protonation energetic. The presence of only small energy barriers, or often, spontaneous transfer of protons from ionic dimmers to produce neutral pairs implies that deprotonation is a fundamental mechanism for triazolium decomposition.

2. Deborah D. Zorn, Jerry A. Boatz and Mark S. Gordon, "Tetrazolium-Based Energetic Ionic Liquids", J. Phys. Chem., <u>B110</u>, 11110 (2006).

This work followed the general approach of that in the previous paper. The cyclic structures are generally the lowest in energy for this species; however, the acyclic for is generally not very much higher in energy. The DFT and MP2 energies are generally in good agreement with each other. An MCSCF π orbital analysis indicates that the electrons in the cation ring are delocalized. Calculated heats of formation show that the tetrazolium cation ring has the potential to release large amounts of energy during decomposition and thus has excellent potential as a high energy fuel. This is especially true when the ring is substituted with $-N_3$ or $-CN$. When a cation is paired with oxygen

rich anions, a single gas phase ion pair was not generally found to be stable. A proton transfers without barrier from the cation to the anion to form a neutral pair.

3. Ian S.O Pimienta, Sherrie Elzey, Jerry A. Boatz and Mark S. Gordon, "Pentazole-Based Energetic Ionic Liquids: A Computational Study", J. Phys. Chem. A, 111, 691 (2007).

The pentazole cation has nitrogen at all positions on the five-member ring. Ionic liquid dimers composed of the five-member monosubstituted pentazole cation and the dinitramide, nitrate, and per chlorate anions were investigated in this work. Of the two monosubstituted pentazole cation isomers, it is predicted that the 1, 3-isomer is lower in energy than the 1, 2-isomer. The relative activation energies and decomposition energies for the decomposition of these cations to N_2 + the corresponding azidinium cation can be related to the electron-donating character of the substituent. An electron-donating substituent tends to increase the activation energy and decrease the decomposition energy. The MCSCF π orbital analysis suggests that the electrons in the cationic pentazole ring are delocalized. The calculated enthalpies of formation show that electron-withdrawing groups such as -CN and -N_3 help to increase the heats of reaction. Several dimer structures composed of the H-substituted pentazole and either of the anions mentioned above are proposed and found to be very unstable. The low barrier connecting the ionic and neutral dimers and the large corresponding exothermicity suggests that a proton is spontaneously transferred to the anion. So, a fundamental step for the decomposition of protonated pentazole is likely to be deprotonation. However, the introductions of additional ion pairs are likely to stabilize the charge separation in the ionic species. It is predicted that the 1-H,2-H-pentazolium-nitrate pair with a barrier for proton transfer of 4.7 kcal/mol is the most stable dimer amongst all of the ion-pairs studied. The ion-pair comprised of the pentazolium cation and perchlorate anion possesses the largest energy content and would have been a desirable high-energy ionic liquid but the 2.7 kcal/mol barrier for proton transfer is prohibitively small for the synthesis and detection of this ionic liquid. The 1-H, 3-H-pentazolium-dinitramide pair is more ideal with a relatively larger barrier of 4.5 kcal/mol and large energy content. Among all the ion-pairs studied, it is calculated that the pentazolium-nitrate pairs provide the largest energy released with a heat of reaction of about 130 kcal/mol.

4. Hui Li, Jerry A. Boatz, and Mark S. Gordon, "Cation-cation Π–Π stacking in small ionic clusters of 1, 2, 4-triazolium", J. Am. Chem. Soc., 130, 392 (2008).

In this paper, a novel combined MP2/CCSD (T) method was used to illustrate that although, as noted above, single cation/anion pairs tend to spontaneously convert to the corresponding neutral pairs, double cation/anion pairs are significantly more stable than the corresponding neutral pairs. In addition, *ab initio* calculations suggest that cation-cation π-π stacking structures can exist in very small ionic clusters such as two 1, 2, 4-triazolium cations and two dinitramide or chloride anions. The structure motifs and interaction patterns provide new understanding of ionic materials with aromatic rings. In

particular, the presence of two ion pairs appears to function like a face of a crystal, resulting in additional stability.

5. Mark S. Gordon, Jonathan M. Mullin, Spencer R. Pruitt, Luke B. Roskop, Lyudmila V. Slipchenko and Jerry A. Boatz, "Accurate Methods for Large Molecular Systems", J. Phys. Chem. (Invited Centennial Feature Article), in press

Three exciting new methods that address the accurate prediction of processes and properties of large molecular systems are discussed. The systematic fragmentaton method (SFM) and the fragment molecular orbital (FMO) method both decompose a large molecular system (e.g., protein, liquid, zeolite) into small subunits (fragments) in very different ways that are both designed to retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources. Each of these methods is inherently scalable and is therefore eminently capable of taking advantage of massively parallel computer hardware, while retaining the accuracy of the corresponding electronic structure method from which it is derived. The effective fragment potential (EFP) method is a sophisticated approach for the prediction of non-bonded and intermolecular interactions. Therefore, the EFP method provides a way to further reduce the computational effort while retaining accuracy, by treating the far field interactions in place of the full electronic structure method. The performance of the methods is demonstrated using applications to several systems, including benzene dimer, small organic species, and pieces of the alpha helix, water, and ionic liquids.

Cryogenic Species. Timothy J. Dudley and Mark S. Gordon, "Theoretical Study of the Formation and Isomerization of Al_2H_2", Mol. Phys., 104, 751 (2006).

There has previously been considerable interest in embedding small, light metals (such as Al) in solid hydrogen. In this work, the lowest-energy singlet and triplet states of the title molecules were studied extensively. This is the first time that all of the minima on the two surfaces have been characterized at the same, high level of theory – multi-reference perturbation theory. Although the singlet surface is generally lower than the triplet surface at the detected stationary point, the energy difference between the two states is less than 20 kcal/mol. The global minimum on the singlet potential energy surface is the di-bridged isomer, with other singlet isomers lying slightly higher in energy. A purely attractive singlet reaction channel involving the insertion of H_2 into the Al-Al bond of an excited Al_2 species is predicted to be exothermic by ~40 kcal/mol.

MCSCF Hessians. Timothy J. Dudley, Ryan M. Olson, Michael W. Schmidt, and Mark S. Gordon, "Parallel Coupled Perturbed CASSCF Equations and Analytic CASSCF Second Derivatives", J. Comp. Chem., 27, 353 (2006).

Because MCSCF wave functions are very important for many applications, as described in the previous paragraph. In order to characterize electronic states at this level of theory, it is important to have analytic second derivatives, Hessians. MCSCF Hessians are also a key first step in the implementation of non-adiabatic coupling (vibronic coupling) matrix elements which are very important for the study of surface crossings (e.g., in

photochemistry). Since MCSCF calculations can be very resource (e.g., time, memory, disk) consuming, it is important to try to reduce these costs. This was accomplished by developing and implementing the MCSCF Hessians as a parallel code. Good scalability up to 128 processors was demonstrated.

GAMESS. Mark S. Gordon and Michael W. Schmidt, "Advances in Electronic Structure Theory: GAMESS a Decade Later", Theory and Applications of Computational Chemistry, Ch.. 41, C. E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria, Eds., Elsevier, 2005.

The electronic structure code GAMESS (General Atomic and Molecular Electronic Structure System) has been supported by AFOSR for ~25 years. In this paper, a description of new developments in GAMESS for the preceding 10 years is presented.